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ACTIVATED CARBON PRODUCTION FROM SPENT MUSHROOM SUBSTRATE FOR SULFIDE REMOVAL

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ABSTRACT

Agriculture industry in Malaysia has evolved entirely over the last decade due to the advancement in science and technology. Also, Malaysia's mushroom industry has also shown an upward trend recently. Thus, the increasing of mushroom production in Malaysia also has led to the increasing of mushroom waste such as the spent mushroom substrate (SMS). It is estimated that for 1 kg of mushrooms grown, about 5 kg of SMS is produced. Since the SMS has high potential to be converted into activated carbon (AC) by pyrolysis method and chemical activation, thus this study is crucial to produce the AC derived from the SMS to be used in industrial application especially in the wastewater treatment as the AC has a very excellent adsorption property. Using AC from SMS, 93.7% of sulfide from the industrial wastewater was successfully removed. The optimum condition to produce AS was at the heating temperature of 515°C and heating time of 106 min.

Keywords: spent mushroom substrate, activated carbon, pyrolysis, sulfide removal.

1. INTRODUCTION

In Malaysia, rubber (39.67%), palm oil (34.56%), rice (12.68%), cocoa (6.75%), and coconut (6.34%) are among the major agricultural crops. Thus, a large amounts of agricultural residues are produced, but these waste are not always utilised for any further downstream operations. Only 27.0% of the wastes are used as fuel in manufacturing and timber industries and the rest are normally disposed of by burning [1].

One of the growing agricultural industries in Malaysia today is the mushroom industry due to the high demand from all over the country. With the increasing production of mushroom, a massive amount of unused spent mushroom waste is produced and has become a huge concern for mushroom growers. Since the information on the use of spent mushroom waste especially the SMS as AC is still scarce in Malaysia, thus this study was deemed necessary. AC can be produced from various carbon-containing feedstocks by the physical or chemical activation of pyrolysedchar. The most common raw materials for the production of AC are the lignocellulosic biomass, anthracite and bituminous coal, lignite, and peat [2].

Agricultural by-products are proven to be promising raw materials for the AC production because of their availability at a low price and compose of high carbon content. AC is versatile and vastly used in different applications, such as adsorbents for waste treatment and pollution control, water purification, catalyst support and dispersion of catalyst, electrochemical systems in batteries, catalyst for oxygen reduction in alkaline electrolyte, and hydrogen storage [3,4,5,6].

The presence of sulfide in wastewater is due to the biological, physical, and chemical processes that usually take place in the submerged part of the sewage collection networks. The sulfide generation rate is affected by several factors such as temperature, pH, concentration of organic materials and nutrients, sulfate concentrations, collection system parameters and performance, and the oxidation reduction potential. Dissolved sulfide could impact the biological processes in wastewater treatment plants. Moreover, the hydrogen sulfide emission can corrode the sewer concrete pipes.The release of awful odours to the atmosphere can be considered toxic to sewer workers and human health, and it pollutes the water supply and environment. In this research, the main objective was tooptimise the AC production and to study the performance for sulfide removal from industrial wastewater.

2. MATERIALS AND METHODS

2.1 Spent Mushroom Substrate (SMS) collection

The SMS used in this research was collected from Rozeriya Enterprise, a frozen food industry located in Kuala Krai, Kelantan, Malaysia. Prior to use, the SMS was dried in an oven at 85°C for 4h.Subsequently, the samples were weighed and recorded. This step was repeated until the weight of the samples was constant as the indication that the samples were totally dried. Then, the sample was ground and sieved to 250 µm for future use.

2.2 Optimization via Design Expert 7

Design Expert 7.0 software was used for the optimisation to determine the best operating condition for the AC production. The factors of heating time (min) and heating temperature (°C) were studied and the sulfide removal (%) was set as the response.

2.3 Experimental set up

2.3.1 Pyrolysis process

In a nitrogen atmosphere, the dried and sieved SMS was heated at a rate of 5 °C/min to the final pyrolysis temperature between 300 and 700°C as obtained from thermogravimetric analysis. Then, the final pyrolysis temperature was maintained for certain duration between 90 and 120 min.

2.3.2 Activation of chars

The chars produced was soaked in KOH solution (42.8 wt%) with a chars/KOH weight ratio of 1:3 on a dry basis. The mixture was kept at 30 °C in an oven for 30 min. Then, the mixture was filtered and the solid obtained was dried. The dried solid was then heated to 800 °C for 90 min in a nitrogen-purged (99.995%) furnace with a heating rate of 10 °C/min. The AC obtained was cooled to room temperature and then washed with 1 M of hydrochloric acid followed with deionised water until the pH of the filtrate became constant.

2.3.3Sulfidesolution preparation

For the preparation of the sulfide solution by considering the degradation of the sulfide, 0.35g of sodium sulfide flake was dissolved in deionised water to make ±30 mg/L of sulfide content. Fifty times dilution was chosen where 2 ml of synthetic wastewater was mixed with 100 ml of deionized water. While for the sulfide removal testing, 20 mL of the diluted sulfide solution was stirred in a beaker at 500 rpm. Then, the AC was added to the solution and stirred for 3 min. The final solution sulfide content was measured. The percentage of sulfide removal was calculated using Equation (1):

$$\% \, removal = \frac{Ci - Cf}{Ci} \, x \, 100 \quad (1)$$

3. RESULTS AND DISCUSSIONS

3.1 Analysis of sample

The SMS was first analysed by TGA to find out the best temperature range for pyrolysis process. From the TGA result shown in Figure-1, the temperature range for pyrolysis process was decided to be between 300 and 700°C.

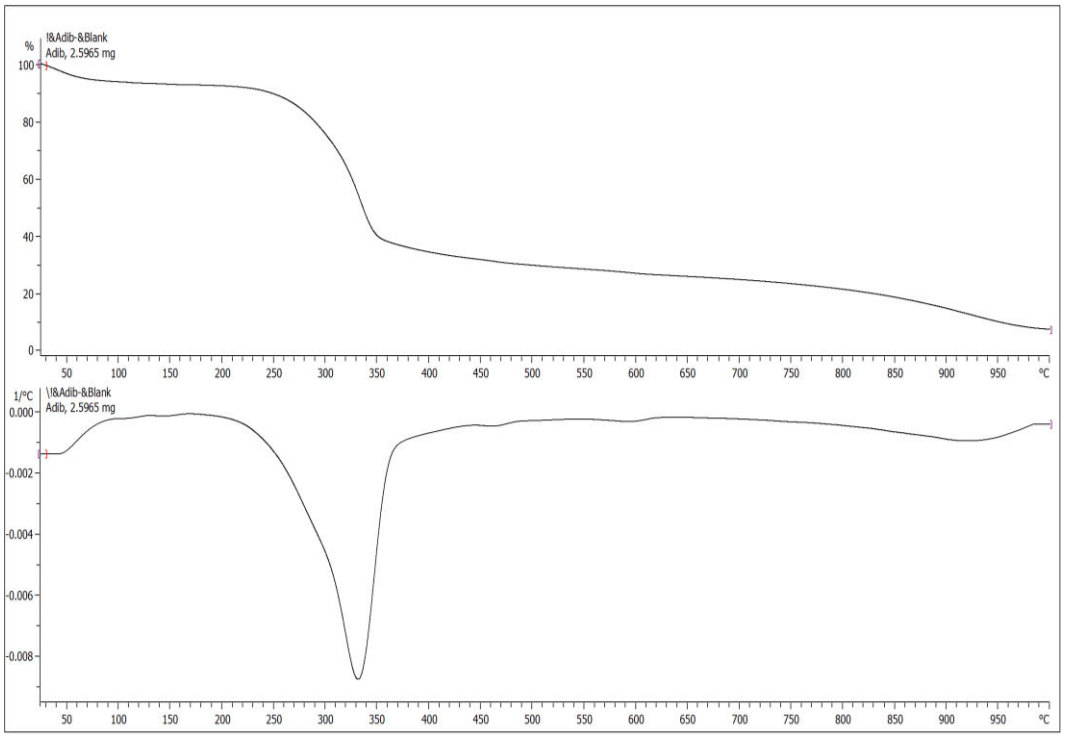

Figure-1. TGA analysis of SMS from 30 to 1,000 °C.

3.2 Sulfide removal

To determine the optimum condition of AC production, the temperature of pyrolysis process and time of pyrolysis were studied. The lowest sulfide removal of 46.61% was obtained at 300°C and 105 min, while the highest sulfide removal of 93.40% was obtained at 500°C and 105 min. Fitting of the data to various models (linear, two factorials, quadratic, and cubic) and the subsequent analysis of variance showed that the sulfide removal using the various ACs produced is most properly described by the quadratic polynomial model The second-order polynomial model used to express the sulfide removal using the various ACs produced as a function of independent variables is shown in Equations2 and 3 in

terms of coded and actual levels, respectively. The analysis of variance from the Design Expert software is shown in Table-1.

$$\text{Sulfide removal (coded)} = 90.10 + 3.62A + 1.06B - 4.31AB - 9.88A^2 - 1.44B^2 \quad (2)$$

$$\text{Sulfide removal (actual)} = -772.58105 + 1.62678A + 8.37105B - 5.74333 \times 10^{-3}AB - 9.87504 \times 10^{-4}A^2 - 0.025512B^2 \quad (3)$$

Table-1. Analysis of variance for the effect of temperature and time in the production of AC from SMS.

Source	Sum of squares	Degree of freedom	Mean square	*F* Value	*p*-value Prob >*F*
Model	2526.44	5	505.29	14.22	0.0015[a]
A – Temp	157.47	1	157.47	4.43	0.0733
B – Time	13.59	1	13.59	0.38	0.5559
AB	74.22	1	74.22	2.09	0.1917
A^2	2234.45	1	2234.45	62.87	<0.0001
B^2	47.19	1	47.19	1.33	0.2870
Residual	248.79	7	35.54		
Lack of Fit	245.33	3	81.78	94.60	0.0004[a]
Pure Error	3.46	4	0.86		
Cor Total	2775.23	12			
R^2	0.9104				
AdjustedR^2	0.8463				

[a] Significant

Table-1 summarises the ANOVA (*F*-test) and *p*-value that are used to estimate the coefficient of the model, to check the significant of each parameter, and to indicate the interaction strength of each parameter. It is observed from the ANOVA that the confidence level is around 95% while the *p*-value of the model is less than 0.0004.

The model with the *p*-value of less than 0.05 is statistically significant, implying that the model is suitable for this experiment. The "Lack of Fit *F*-value" of 94.60 implies that it is significant. There is only a 0.04% chance that the value this large could occur due to noise. Significant lack of fit was bad; we want the model to fit. Things to consider are model reduction, response transformation, and/or outliers. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 11.542 indicates an adequate signal. This model can be used to navigate the design space.

The coefficient of determination (R^2) and adjusted coefficient of determination (adjusted R^2) are 0.9104 and 0.8463, respectively, which indicate that the estimated model fits the experimental data satisfactorily. Lee *et al*. (2010) suggested that for a good fit of a model, R^2 should be at least 0.80. The R^2 for these response variables is higher than 0.80, indicating that the regression models explained the mechanism well. Meanwhile, Figure-2 shows the plot of the actual versus predicted data while Figure-3 shows the normal plot of residuals.

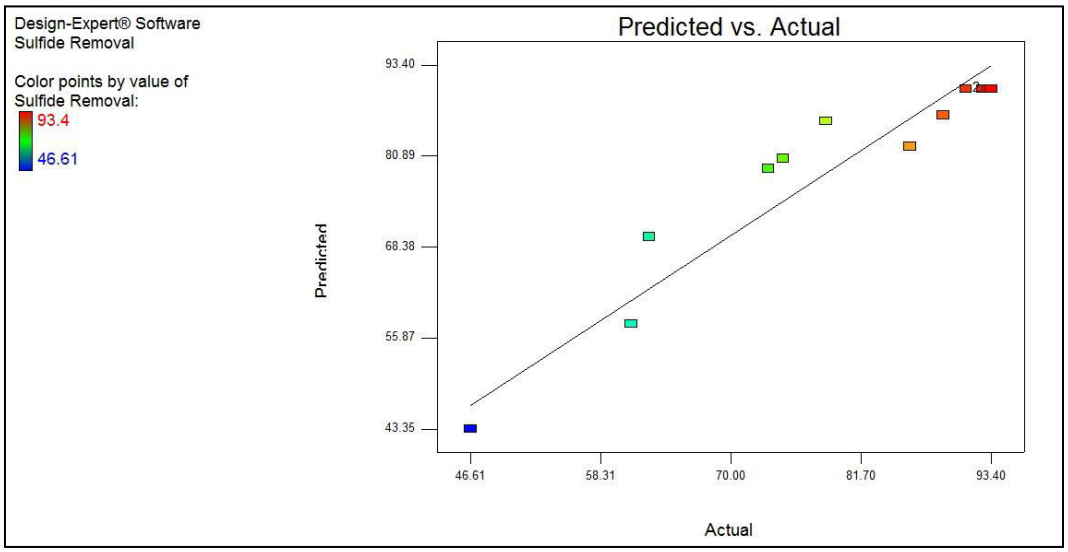

Figure-2. Graph of predicted vs actual data.

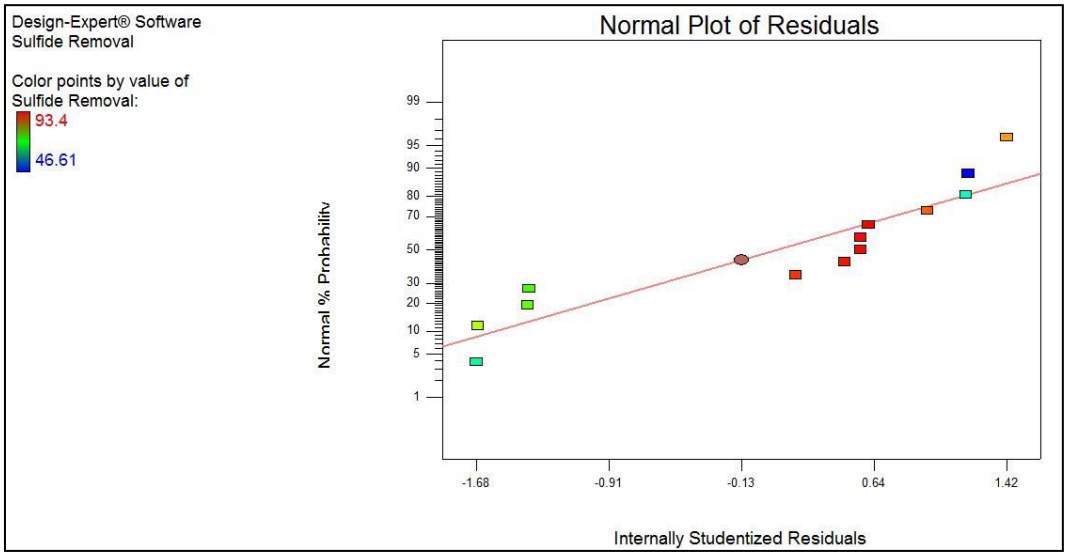

Figure-3. Graph of normal plot of residuals.

A linear distribution is observed which is indicative of a well-fitting model. The values predicted were close to the observed values of sulfide removal. The plot indicates that the difference between actual and predicted values follow a normal distribution and forms an approximately straight line. From Table-1, the *p*-value of factor A (temperature) of 0.0733 is smaller than that of factor B (time) of 0.5559. These values proved that temperature was the main factor affecting the sulfide removal. The effect of temperature to sulphide removal is shown in Figure-4.Meanwhile, the contour and three-dimensional (3D) surface plots of the data are shown in Figures 5 and 6, respectively.

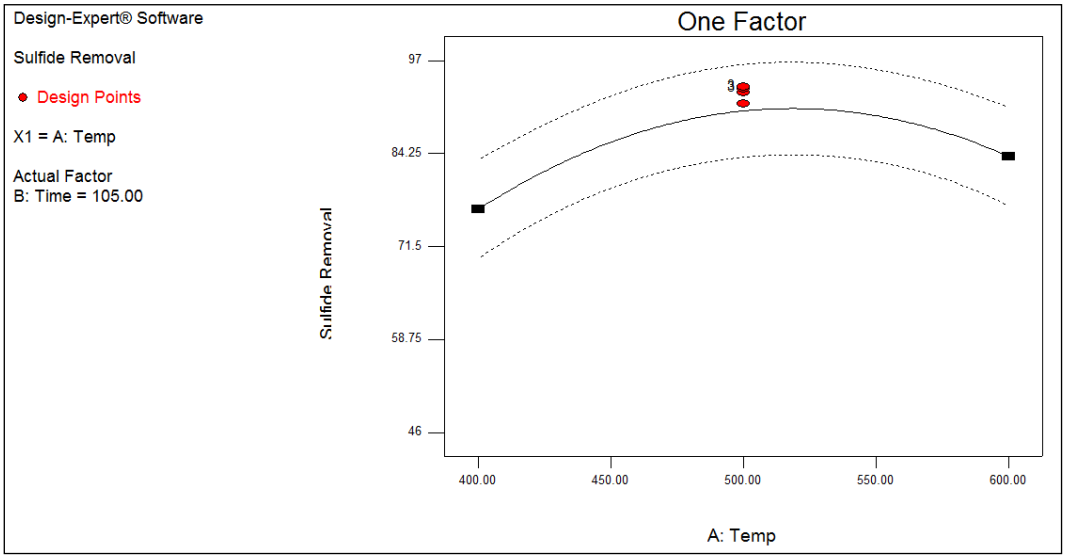

Figure-4. Graph of temperature versus sulfide removal.

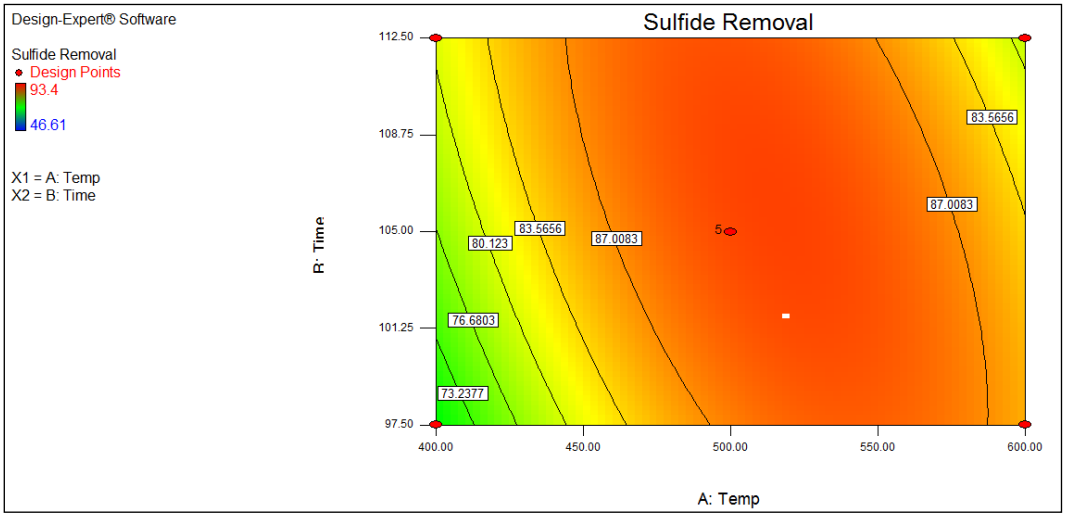

Figure-5. Contour plot of the data.

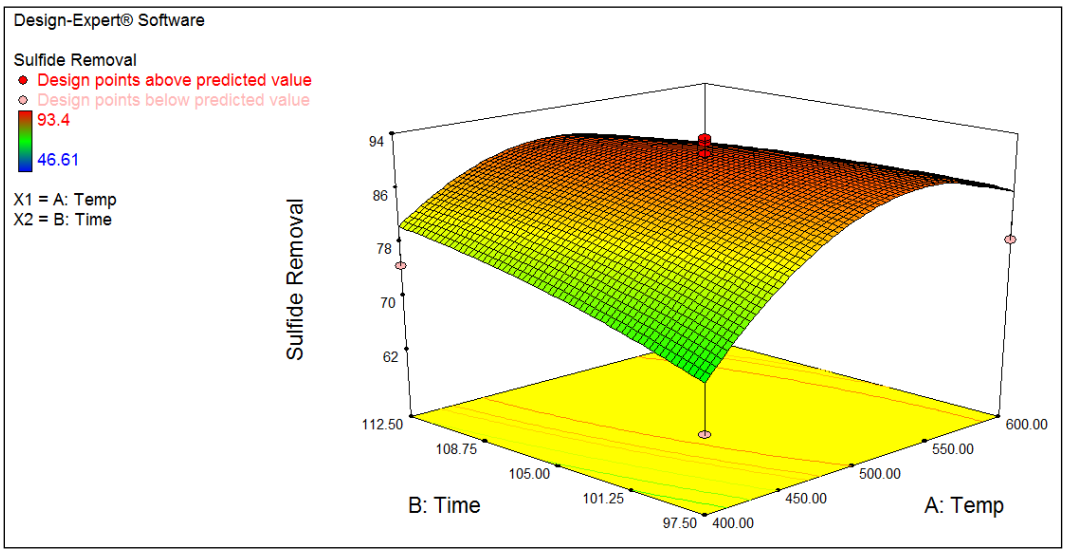

Figure-6. 3D surface plot of the data.

The plotted data depicts that the sulfide removal was the highest at 93.4%. The effect of sulfide removal is more significantly affected by the change of temperature as shown in Figure-4. The effect may be attributed to the number and size of pores during heating, where at the optimum condition, the reaction was high and produced a better activated carbon.

3.3 Characterisation of optimised AC

3.3.1 Scanning electron microscopy (SEM)

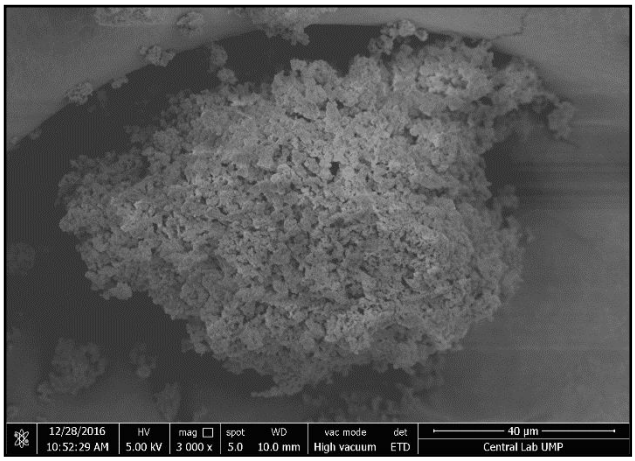

Figure-7. Magnification 3,000×.

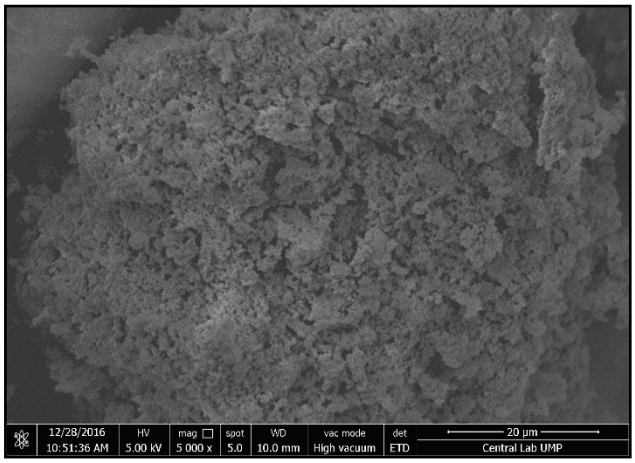

Figure-8. Magnification 5,000x.

Figures 7 and 8 show the SEM images of the optimised AC produced at 515°C. Different pyrolysis temperature can cause substantial changes to the surface morphology of the AC. From these figures, the AC had a rough surface with many pores and deep crack due to the dramatic release of different volatile compounds as the temperature was increased, leading to the formation of its loose structure.

3.2.2 Fourier transform infrared (FTIR)

FTIR spectrum for the activated carbon obtained is shown in Figure-9. The functional groups identified from the FTIR are given in Table-2.

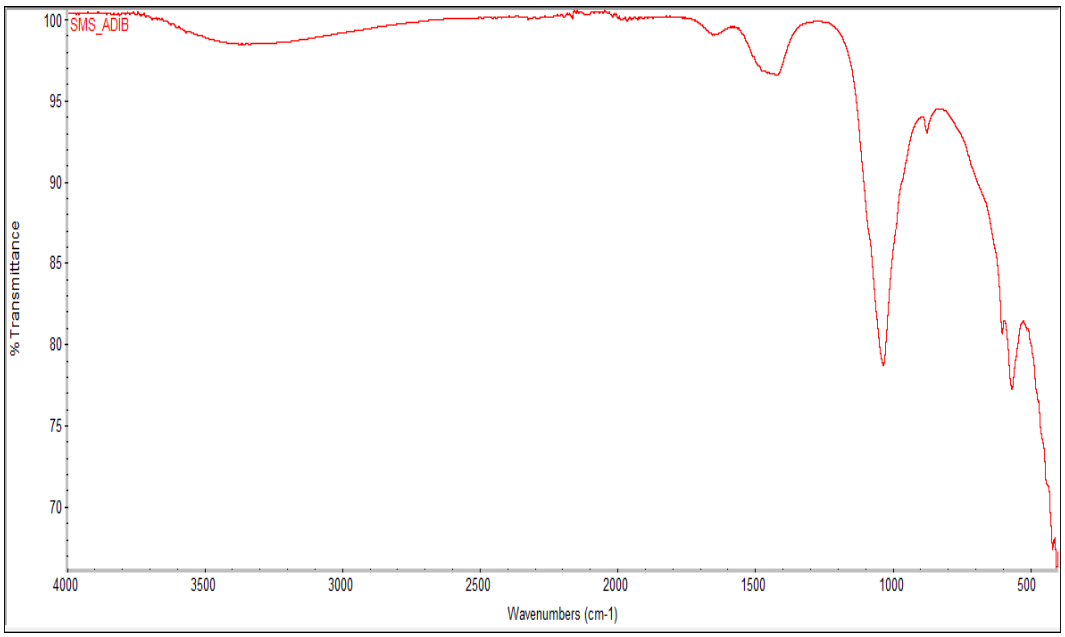

Figure-9. FTIR spectrum of activated carbon.

A small peak at around 3,400 cm^{-1}indicates the complete volatilisation of oxygen-containing groups due to the high pyrolysis temperature. Meanwhile, absorption peak at 1,600 cm^{-1}indicates the presence of polynuclear aromatic compounds. However the intensity of the peak is small. The absorption peaks at 1,400 and 850 cm^{-1} represent the aromatic C-H vibration. The intensity of the absorption peak at 1,050 cm^{-1} is the highest, which is

attributed to C-O stretching. Since SMS has high oxygen content, this phenomenon can be explained by the possibility that the intense interaction between oxygen and carbon during pyrolysis led to the firm combination.

Table-2. Infrared band assignments for the chars.

Wave number (cm^{-1})	Description
3,420	-OH stretching in phenols and alcohols
2,925	Aliphatic CH_3 stretching in alkanes
2,850	Aliphatic CH_2 stretching in alkanes
2,360	C=O asymmetric stretching vibration of CO_2
1,635	C=O stretching (acid, aldehyde, and ketone)
1,590	In-plane skeletal vibrations in aromatic rings
1,416	Aromatic C-H vibration
1,315	In-plane bending vibration of phenolic -OH
1,049	C-O (anhydrides) stretching
873	Out-plane bending vibration of aromatic C-H

3.2.3 Surface area analysis (BET)

The N_2 adsorption/desorption isotherm is shown in Figure-10. The optimised AC showed an isotherm that is similar to Type I-B as defined by IUPAC, indicating the presence of a complex micropore structure. Moreover, they contained no distinct plateaus even at high relative pressure because some mesopores resulted in a more enhancement near saturation. At higher relative pressure, the hysteresis loop (Type H_4) is indicative of slit-shaped pores. The BET surface area and total pore volume of the optimised AC were 51.7755 m^2/g and 0.002537 cm^3/g, respectively.

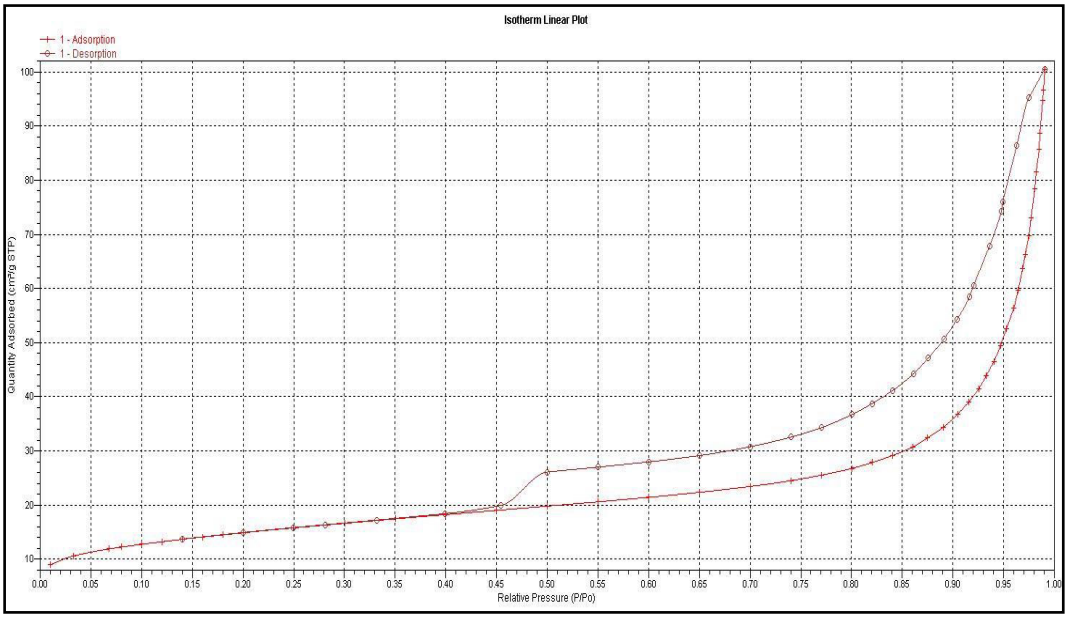

Figure-10. N_2 adsorption/desorption isotherm of the optimised AC.

CONCLUSIONS

It can be concluded that the highest sulfide removal of 93.7% can be achieved by the AC produced at the optimum condition of heating temperature of around 515°C and heating time of around 106 min. The final sulfide removal percentage of the activated carbon produced was achieved based on the optimisation work and the validation experiments were run three times to ensure the results obtained are consistent with the proposed model developed with the aid of Design Expert 7.

ACKNOWLEDGEMENT

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REFERENCES

[1] Rosmiza M, Davies W, Aznie R C, Jabil M andMazdi M. 2016. Mediterranean Journal of Social Sciences. 7: 406.

[2] Pollard SJT, Fowler GD, Sollars CJ and Perry R. 1992.The Science of the Total Environment. 116: 31.

[3] Kaouah F, Boumaza S, Bearrama TandTrari M. 2013. J. Clean. Prod. 54: 296.

[4] Liu Y, Guo Y, Gao W, Wang Z, Ma YandWang Z, J.Clean. Prod. 32(2012): 204.

[5] Ioannidou O and Zabaniotou A. 2012. Renewable and Sustainable Energy Reviews. 11: 1966.

[6] Ma Y, Wang Q, Sun X, Wang X, Su W and Song N. 2014.BioResources. 9: 3939.